Electronic Supplementary Material (ESI) for Nanoscale.

On the Role of Localized Surface Plasmon Resonance in VU-Vis Light Irradiated Au/TiO_2 Photocatalysis System: Pros and Cons

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Supporting Information

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I. Simulation Details of Absorption Cross Section Spectrum, Electric Field Intensity Maps and Charge Density Maps

Simulations of the absorption cross section spectrum were performed using the finite element method (FEM) implemented in COMSOL Multiphysics 4.2 software, which has been proven particularly useful for simulating the optical properties of complex morphologies.[1] And the simulations were run on a quad core Intel i7-4790 3.6 Ghz processor with 16 GB of RAM. Fine meshing entails a maximum element size of 15.6 nm, a minimum element size of 0.66 nm, and a maximum element growth rate of 1.35. The diameters of the gold nanoparticle and the titanium dioxide nanoparticle were 10 nm and 50 nm, respectively. In addition, the Au NPs and Au-TiO_2 were modeled in water (n = 1.33) environment and water (n = 1) environment, respectively.

Based on the Drude model, the dielectric function ε(ω) of the gold can be expressed as[2],

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\frac{\omega}{\tau}} \tag{1}$$

Here τ is the relaxation time of the free electron and ω_p is the plasma frequency of the bulky metal as given by $\omega_p = \sqrt{n_e e^2 / \varepsilon_0 m^*}$, with n_e being the number density of electrons, e the electric charge, and m∗ the effective mass of the electron. For gold, $\omega_p = 2.183 \times 10^{15}$Hz, $\tau = 155 \times 10^{-15}$ s. The dielectric constant of TiO_2 nanoparticles used in the calculation were obtained from [3].

II. I-V Characteristics of Bare TiO_2 and the CAFM tip

Whether the CAFM tip in contact with bare TiO_2 can form the Schottky contact was unclear. Therefore, we should measure the I-V characteristics of bare TiO_2 by CAFM. As shown in figure S2, it is obvious that the contact of tip and bare TiO_2 is the ohmic contact.

III. Calculation Details of Schottky Barrier High and Ideality Factor

Firstly, The ideality factor n is determined from the slop of the linear region of the forward bias ln(*I*)-*V* characteristics through the relation as,

$$n = \frac{q}{kT}\left(\frac{dU}{d(\ln I)}\right) \tag{2}$$

Where *U* is the applied bias voltage, *k* is Boltzmann constant, *T* is the temperature in Kelvin, *q* is the charge of the electron. Then based on the relation as,

$$U = \frac{kTn}{q}\ln I - \frac{kTn}{q}\ln I_0 \tag{3}$$

We could know that $\left(-\frac{kTn}{q}\ln I_0\right)$ was equal to the intercept of ln(*I*)-*V* characteristic curve. Therefore, if n have been determined, I_0 also could be obtained. By taking the natural logarithm of Eq.(1) in text, Schottky barrier high Φ_{b0} can obtain,[4]

$$\phi_{b0} = -kT\ln\left(\frac{I_0}{T^2}\right) + kT\ln\left(AA^*\right) \quad (4)$$

Here S is the contact area, A^* is the effective Richardson constant.

IV. References for the Supporting Material

(1) Liu, J.; Wang, X.; Lin, Z.; Cao, Y.; Zheng, Z.; Zeng, Z.; Hu, Z., *Electrochimica Acta* 2014, 136, 66-74.

(2) Zhang, X.; Chen, Y. L.; Liu, R. S.; Tsai, D. P., *Reports on progress in physics. Physical Society* 2013, 76, 046401.

(3) Seh, Z. W.; Liu, S.; Low, M.; Zhang, S.-Y.; Liu, Z.; Mlayah, A.; Han, M.-Y., *Advanced materials* 2012, 24, 2310-2314.

(4) Dökme, I., *Microelectronics Reliability* 2011, 51 360-364.

V. Supporting Figures

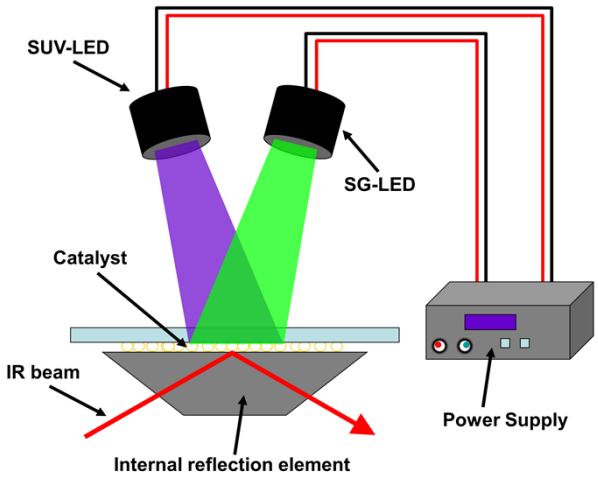

Figure S1. Scheme of the ATR-FTIR cell, including the SUV-LED and SG-LED

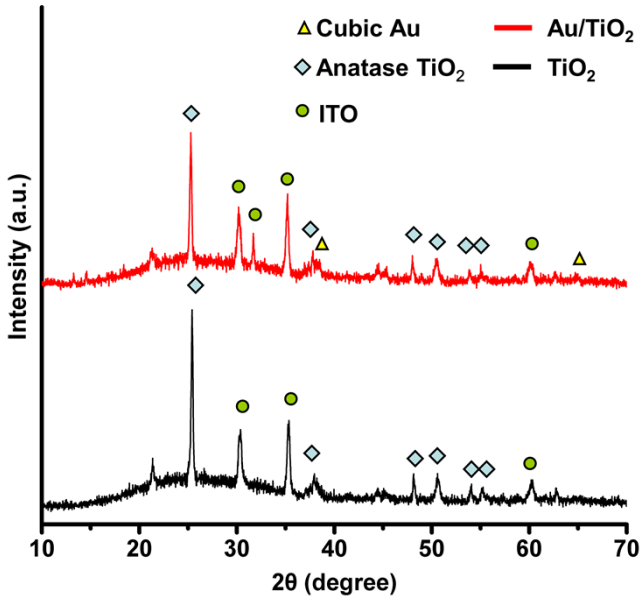

Figure S2. The X-ray diffraction patterns for TiO_2, Au-TiO_2. The plots are offset for clarity; peak positions for Au (△) and TiO_2 (◇), ITO (○) are indicated.

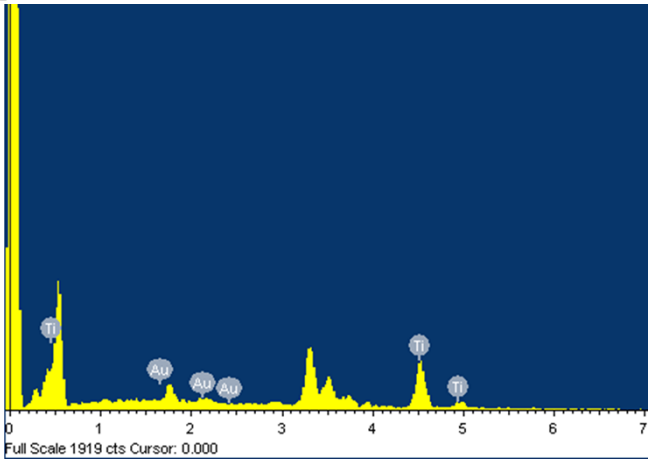

Figure S3. The EDS profile of Au/TiO_2

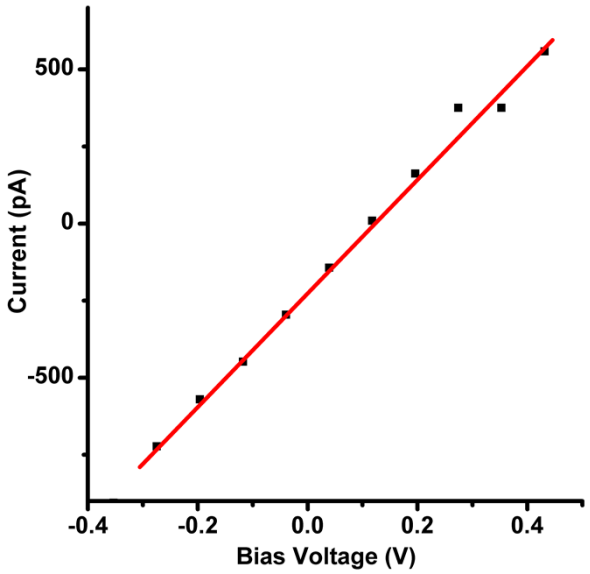

Figure S4. The *I-V* curves of the contact between CAFM tip and bare TiO_2